



Phase behavior of a cell fluid model with Curie-Weiss interaction

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INTRODUCTION

In [1,2], we introduced a simple Curie-Weiss type model of a single-sort continuum particle system in which space \mathbb{R}^d is divided into congruent (cubic) cells. For a bounded region $V \subset \mathbb{R}^d$ consisting of N_v such cells, the attraction between each two particles in V is set to be g_a/N_v , regardless of their positions. If such two particles lie in the same cell, they repel each other with intensity $g_r > g_a$. Unlike [3], we deal with the grand canonical ensemble. We proved (see [1,2]) the possibility of a strict transition from a continuous system of interacting particles to such a cell model and the exact calculation of its grand partition function. As a result, the existence of a *cascade of first-order phase transitions* in the cell model with the Curie-Weiss interaction is strictly mathematically proved. Now we refer to the exact calculation of the equation of state of the model (see [1,2] for details) and focus on important additions to the existing results of analytical calculation and quantitative analysis of the phenomenon.

THE MODEL

The **equation of state (EoS)** is a good tool for studying the properties of any system, e.g. obtained from the ratio

$$PV = k_B T \ln \Xi,$$

where P is the pressure of a system, V is its total volume, k_B is the Boltzmann constant, T is the temperature, and Ξ is the **grand partition function (GPF)**. In the case of a continuous system of N interacting particles, the GPF has the form [4]

$$\Xi = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_V dx_1 \dots \int_V dx_N \exp \left[-\frac{\beta}{2} \sum_{x,y \in \eta} \Psi_{\Lambda}(x,y) \right],$$

here $z = \exp(\beta\mu)$ is the activity, μ is the chemical potential, $\beta = (k_B T)^{-1}$ is the inverse temperature, $\eta = \{x_1, \dots, x_N\}$, x_i are the coordinates of the i -th particle. If the system volume conditionally divided into a finite number of congruent mutually disjoint cubic cells $\Delta_l = (-c/2, c/2]^3 \subset \mathbb{R}^3$, each of volume $v = c^3 = V/N_v$, the potential energy is written as [2]

$$\sum_{x,y \in \eta} \Psi_{\Lambda}(x,y) = \sum_{l_1, l_2 \in \Lambda} U_{l_1 l_2} \rho_{l_1}(\eta) \rho_{l_2}(\eta),$$

here $\rho_l \eta = \sum_{x \in \eta} I_{\Delta_l}(x)$ is the occupation number of an l -th cell. Here I_{Δ_l} is the indicator of Δ_l , that is, $I_{\Delta_l}(x) = 1$ if $x \in \Delta_l$ and $I_{\Delta_l}(x) = 0$ otherwise.

THE POTENTIAL OF INTERACTION $U_{l_1 l_2}$

$$U_{l_1 l_2}(x,y) = \begin{cases} -\frac{g_a}{N_v}, & x \in \Delta_{l_1}, y \in \Delta_{l_2}, l_1 \neq l_2; \\ g_r, & x, y \in \Delta_l \end{cases}$$

$g_r > g_a > 0$ [1] is the condition of stability.

Optimization of thermodynamic variables: $p = \beta g_a$ $f = g_r/g_a$

SOLUTION OF THE GPF

Asymptotic solution of the GPF in the case of Curie-Weiss interaction is

$$\Xi = \exp(N_v E_0(\bar{z}, \mu)),$$

$$z = \bar{z} \quad \text{when} \quad E_0(z, \mu) = \max E_0(z, \mu),$$

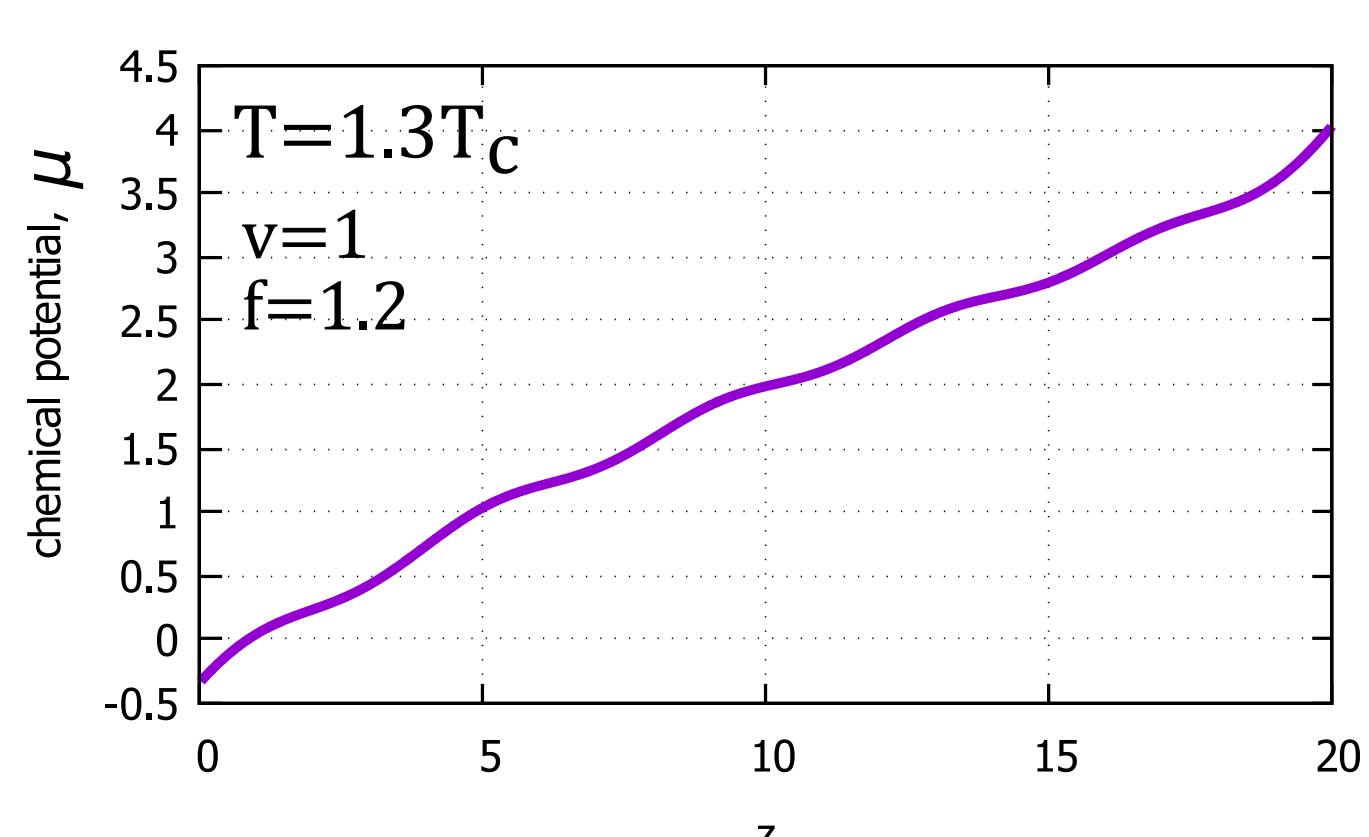
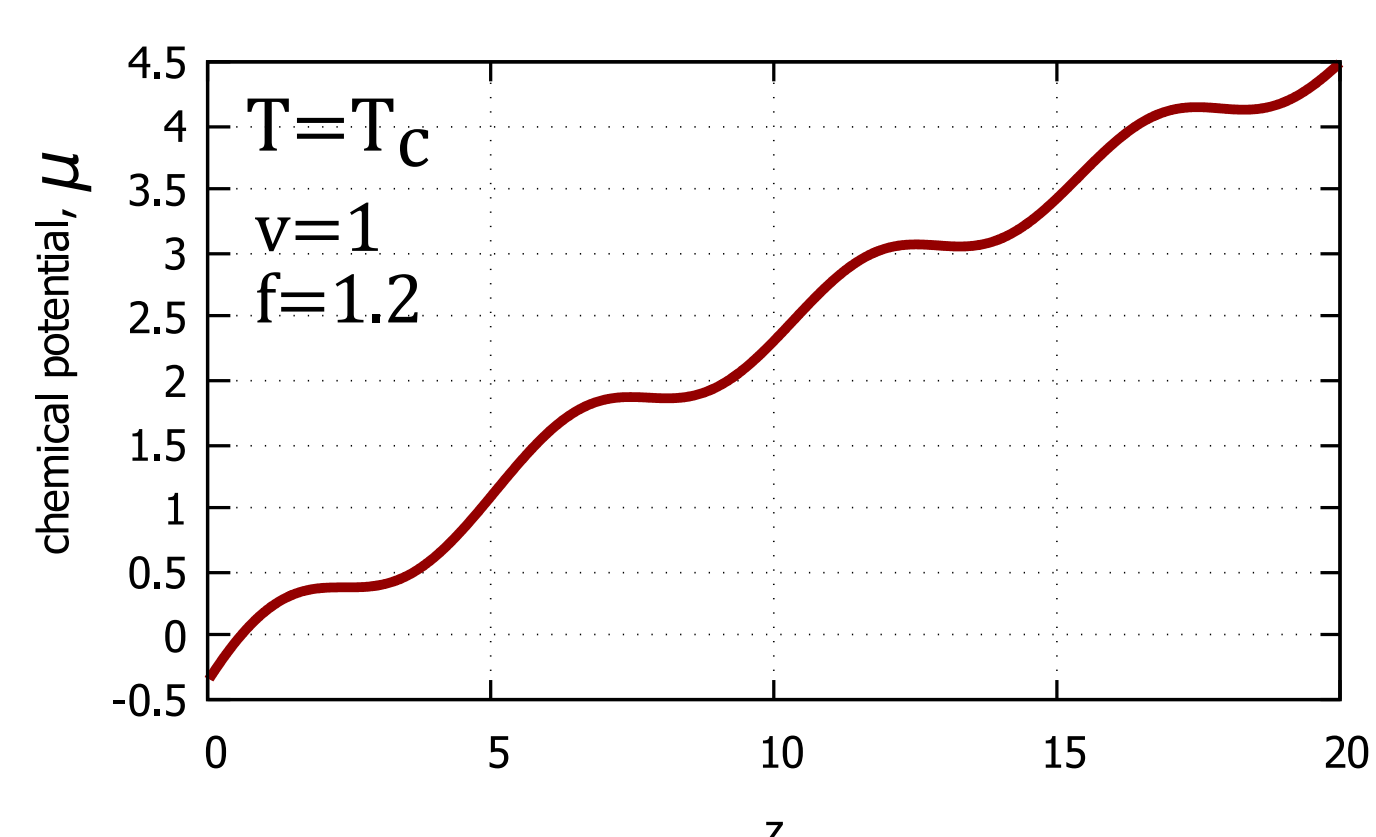
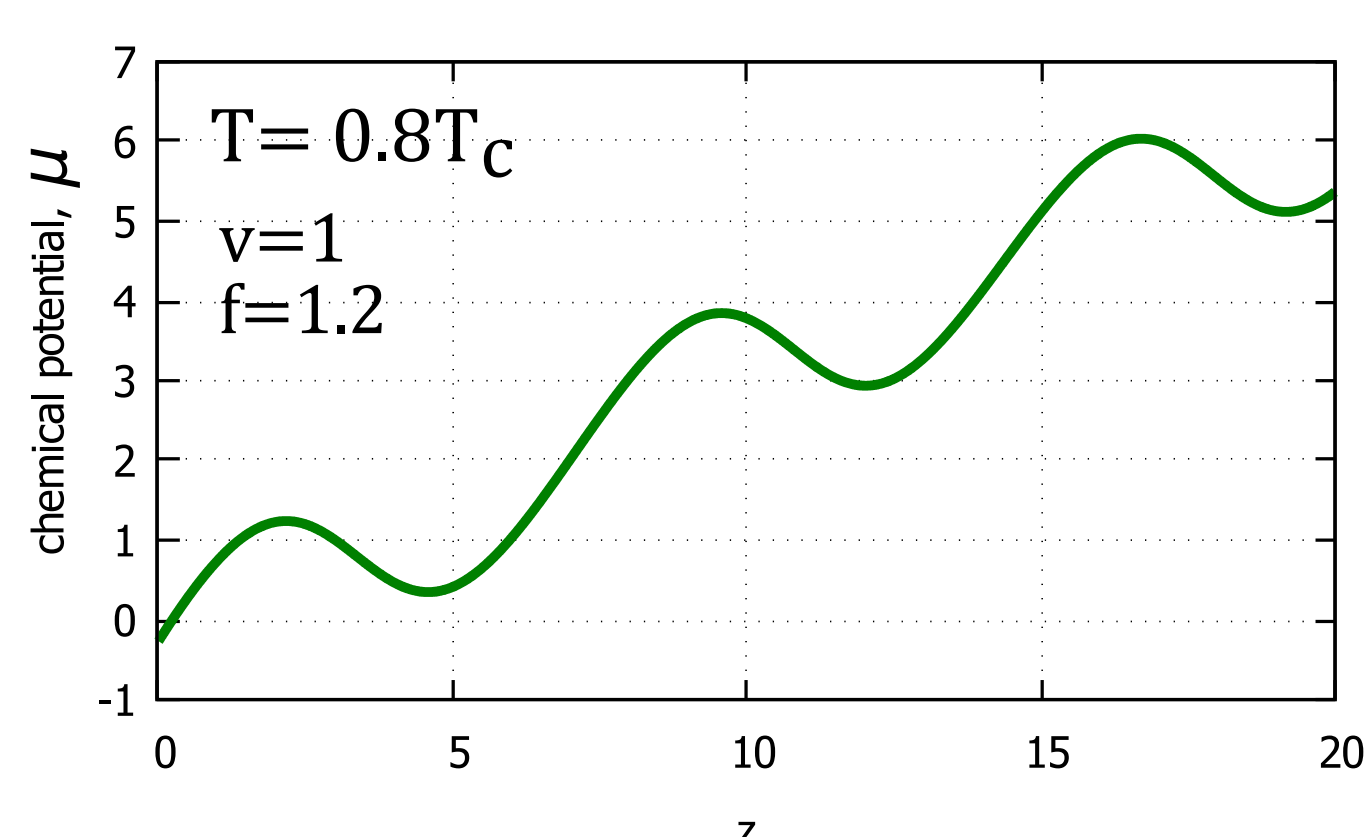
$$E_0(\bar{z}) = \ln K_0(\bar{z}) - \frac{p}{2} \left(\frac{K_1(\bar{z})}{K_0(\bar{z})} \right)^2.$$

$K_m(z)$ are the special functions

$$K_m(z) = \sum_{n=0}^{\infty} \frac{v^n}{n!} n^m \exp\left(-\frac{fp}{2} n^2\right) \exp(zn)$$

BEHAVIOR OF THE CHEMICAL POTENTIAL

$$\frac{\partial E_0(z, \mu)}{\partial \mu} = 0, \quad \Rightarrow \quad \beta\mu = \bar{z} - p \frac{K_1(\bar{z})}{K_0(\bar{z})}$$



AVERAGE DENSITY

$$\eta = \frac{\langle N \rangle}{V} = \frac{\bar{n}}{v} \quad \bar{n} = \frac{1}{N_v} \frac{\partial \ln \Xi}{\partial \beta \mu} \quad \bar{n} = \frac{K_1(\bar{z})}{K_0(\bar{z})}$$

PARAMETERS OF THE CRITICAL POINT

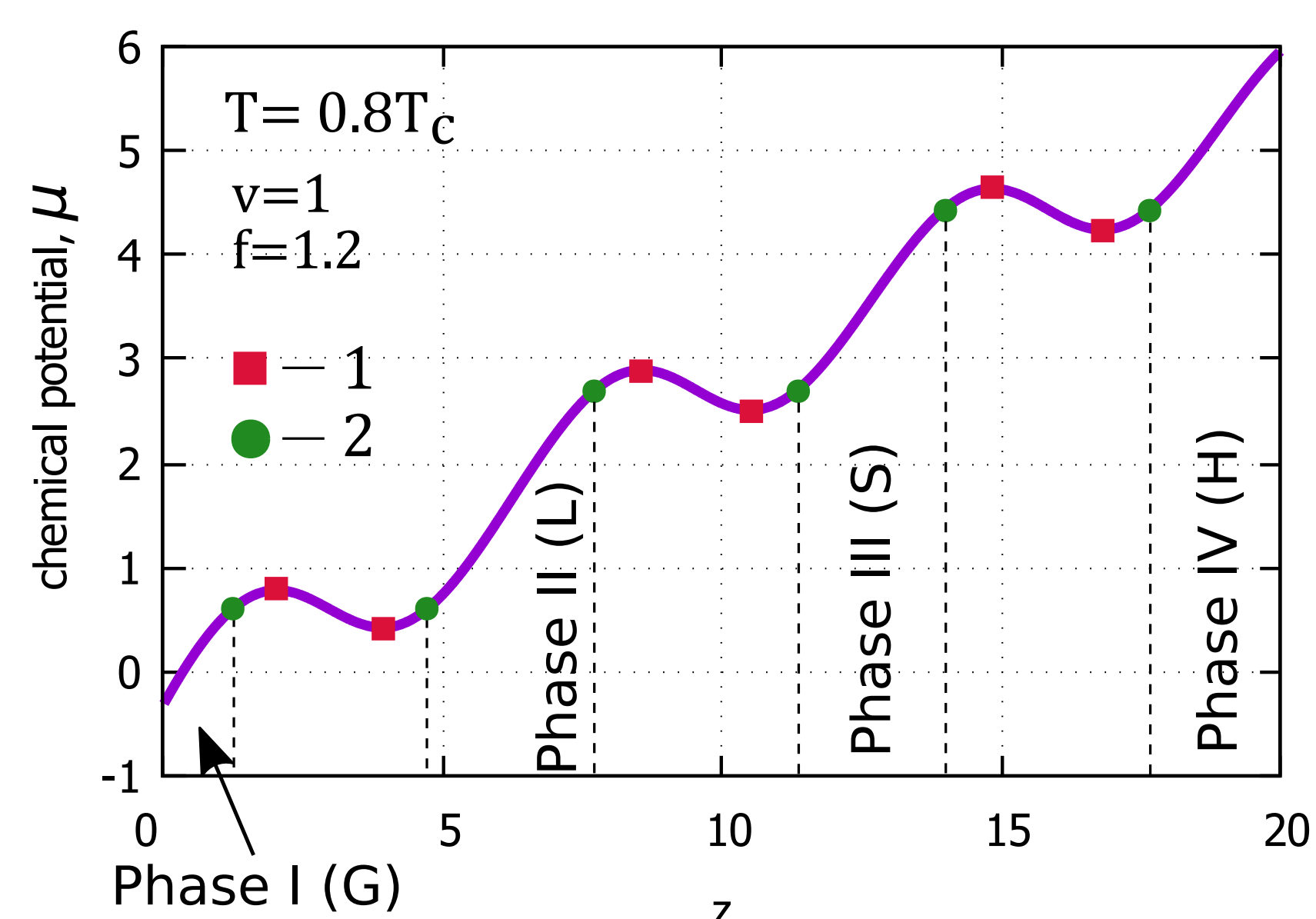
Condition for the inflection points of the function $\mu(\bar{z})$ at $T = T_c$ is the solution of

$$\begin{cases} \frac{\partial \mu}{\partial z} = 0, \\ \frac{\partial^2 \mu}{\partial z^2} = 0 \end{cases}$$

Parameters of the inflection points for first three (n) phase transitions in the cascade ($v = 1, f = 1.2$)

(n)	$p_c^{(n)}$	$z_c^{(n)}$	$n_c^{(n)}$
1	3.9282	2.3983	0.5139
2	3.8185	7.5829	1.5056
3	3.7699	12.4174	2.5030

EXTREMA AND GLOBAL MAXIMA



1. Extrema points of the chemical potential

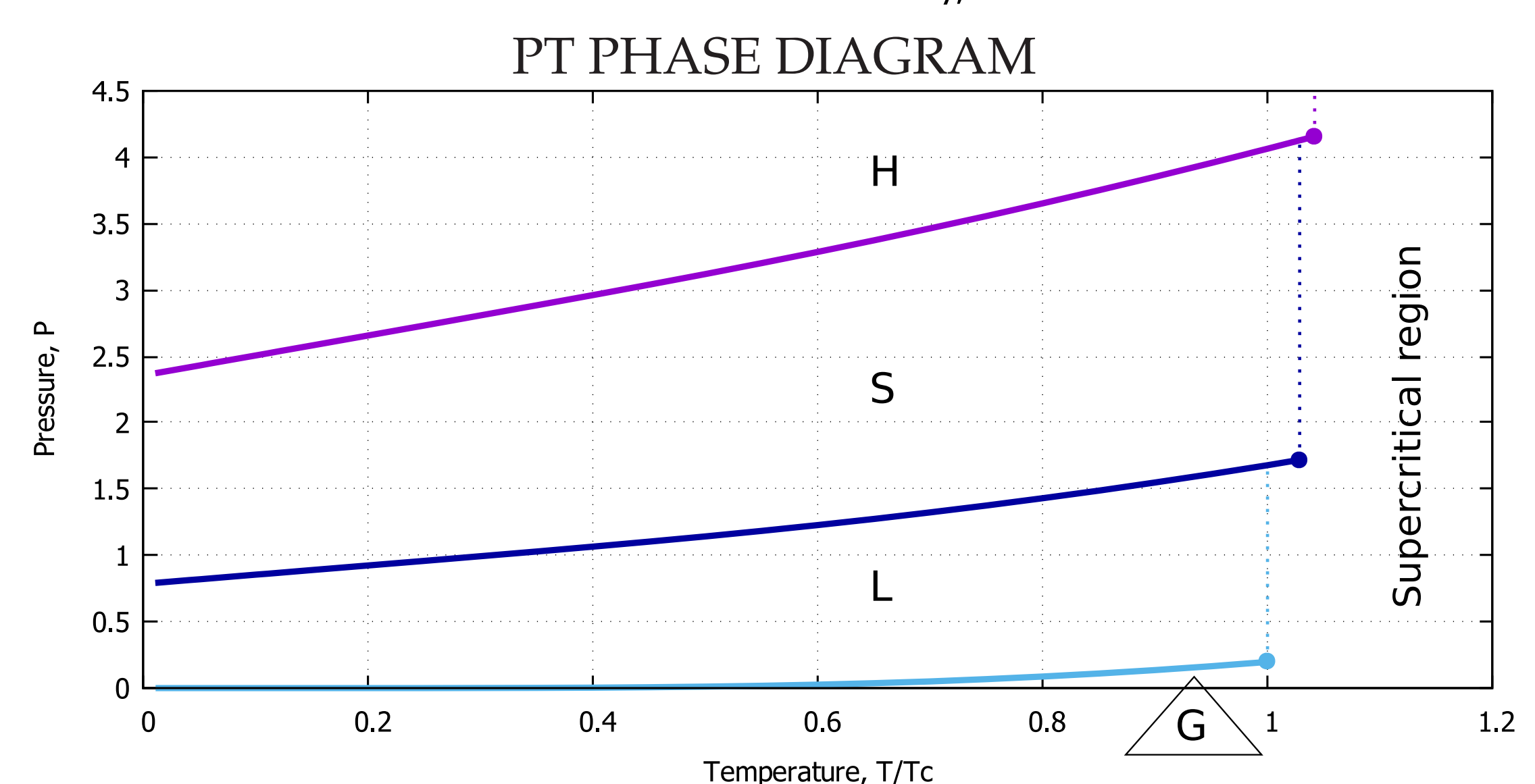
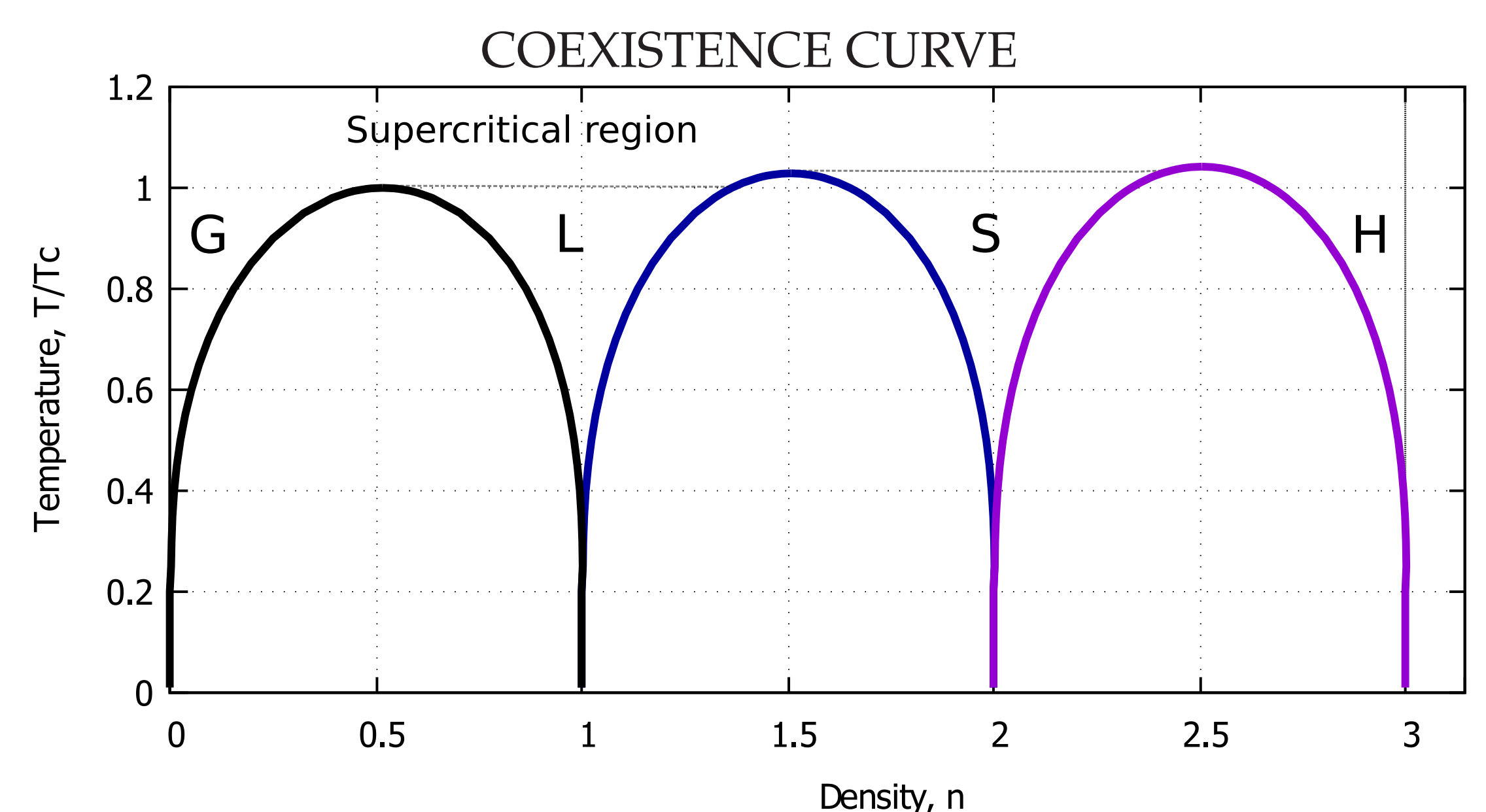
$$\frac{\partial \mu}{\partial z} = 0$$

2. Global maxima points of the chemical potential

$$\begin{cases} E_0(z_1) - E_0(z_2) = 0, \\ \mu(z_1) - \mu(z_2) = 0 \end{cases}$$

PHASE DIAGRAMS

$$\text{Equation of state} \quad Pv = k_B T \ln K_0 - \frac{p}{2\beta} \bar{n}^2$$



CONCLUSIONS

- An accurate calculation shows that a one-component cell model with Curie-Weiss potential has a sequence of first order phase transitions at temperatures below the critical one. Emergence of such a cascade is possibly associated with the point nature of particles. The appearance of phases with higher and higher density in such a model is due to the lack of a term in the potential of interaction that would prohibit the excess concentration of particles in the cell.
- We derived conditions and relations for the values of the critical point parameters. We analyzed the mechanism of phase transitions based on the behavior of the chemical potential as a function of density.
- The obtained phase diagram confirms the absence of a triple point in such a system.

REFERENCES

- [1] Kozitsky Yu., Kozlovskii M. and Dobush O., In Modern Problems of Molecular Physics, pgs 229-251. Springer, 2018.
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- [4] Hill, T.L. An introduction to statistical thermodynamics. Courier Corporation, 1986.